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Preliminary communication

Two crystalline toluene-soluble 1,2-organobis(phenylphosphido)dilithium compounds. The monomeric $1,2\text{-}C_6H_4(PPh)_2[Li(TMEDA)]_2$ and the dimeric $[(PhPCH_2CH_2PPh)\{Li(THF)_2\}_2]_2$ *

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Abstract

Treatment of $1,2\text{-}C_6H_4(PHPh)_2$ with $LiBu^n$ in $n\text{-}C_6H_{14}$ and TMEDA (TMEDA $= Me_2N[CH_2]_2NMe_2$) affords $1,2\text{-}C_6H_4(PPh)_2[Li(TMEDA)]_2$, which both in the crystal (Li–P 2.58(3) and 2.55(3) Å) and in PhMe solution ($J(^{31}P\text{-}^{7}Li)$ 36 Hz) has a monomeric structure with each Li bound to two equivalent P atoms and each P to two equivalent lithium atoms, and yields $\overline{SnR_2[P(Ph)C_6H_4PPh}\text{-}1,2]$ (crystalline *rac* when $R = CH(SiMe_3)_2$; *rac* + *meso* when R = Me) on treatment with SnR_2Cl_2 or *rac* + *meso*-$1,2\text{-}C_6H_4[P(Ph)SiMe_3]_2$ on treatment with $SiClMe_3$. By contrast, $1,2\text{-}C_2H_4(PPh)_2[Li(THF)_2]_2$ (THF = tetrahydrofuran) is an $(LiP)_4$-skeletal dimer both in the solid and in PhMe ($J(^{31}P\text{-}^{7}Li)$ 39 and 47 Hz).

Di(organo)phosphidolithium reagents $[Li(PR_2)L_m]_n$ are of structural interest (X-ray data are available for several compounds, the first being reported in 1983) [1,2] and of value as $\bar{P}R_2$-transfer reagents to electrophilic sites. Bifunctional compounds have received scant attention, although other compounds of type $(LiX)_2Y$ are of theoretical concern [3]. Nevertheless, some of them are useful synthons: e.g. $Li_2(PhPCH_2CH_2PPh)$ for phosphorus macrocycles (these ligands are obtained without stereoselectivity at the P-centres) [4a], and $Li_2[C_6H_4(PPh)_2\text{-}1,2]$ for benzotriphosphole [4b].

We now report the X-ray structure of the crystalline monomeric $1,2\text{-}C_6H_4(PPh)_2[Li(TMEDA)]_2$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) (**1**) [11 **], which has each lithium atom bound equivalently to two phosphorus

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* No reprints available

** References numbers with asterisks indicate notes in the list of references.

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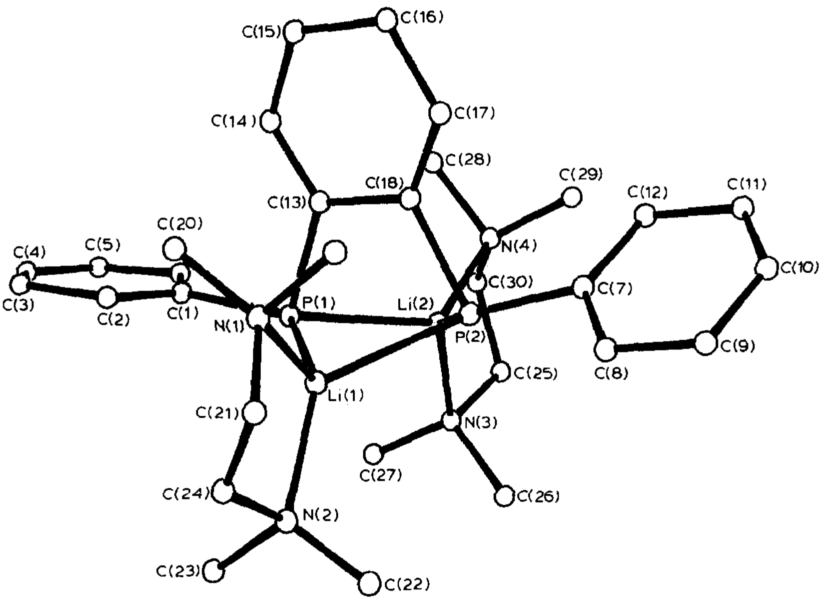


Fig. 1. The molecular structure and atom numbering scheme for $1,2\text{-}C_6H_4(PPh)_2[Li(TMEDA)]_2$ (**1**); for selected data, see Table 1.

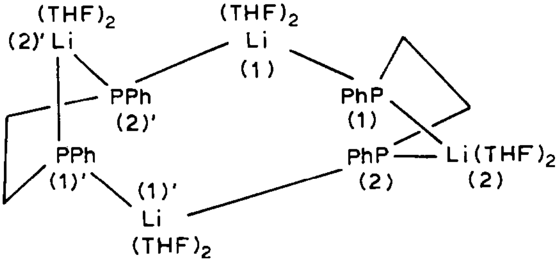
atoms. Fig. 1; the two lithium atoms are on opposite sides of the planar $1,2\text{-}C_6H_4P_2$ moiety and the overall configuration of **1** resembles that of $1,2\text{-}C_6H_4(CHSiMe_3)_2[Li(TMEDA)]_2$ [5]. This is among the first crystalline monomeric LiP$<$ compounds; cf. also $1,2\text{-}C_6H_4(PPh)_2PLi(THF)_3$ $LiPPh_2(PMDETA)$ [2b] (PMDETA = $[Me_2NCH_2CH_2]_2NMe$), whereas $[Li(12\text{-crown-}4)_2][PPh_2]$ has well separated ions [6], and $[Li(\mu\text{-}PPh_2)(TMEDA)]_2$ is a dimer [2b]. There is a further contrast (Table 1) with the crystalline dimeric Li_4P_4 macrocycle $[(PhPCH_2CH_2PPh)\{Li(THF)_2\}_2]_2$ (THF = tetrahydrofuran) (**2**) [7].

From variable temperature $^{31}P\{^1H\}$ and $^7Li\{^1H\}$ NMR data [12 *] we conclude that the structure of **1** in toluene-d_8 solution at low temperature is identical to that

Table 1

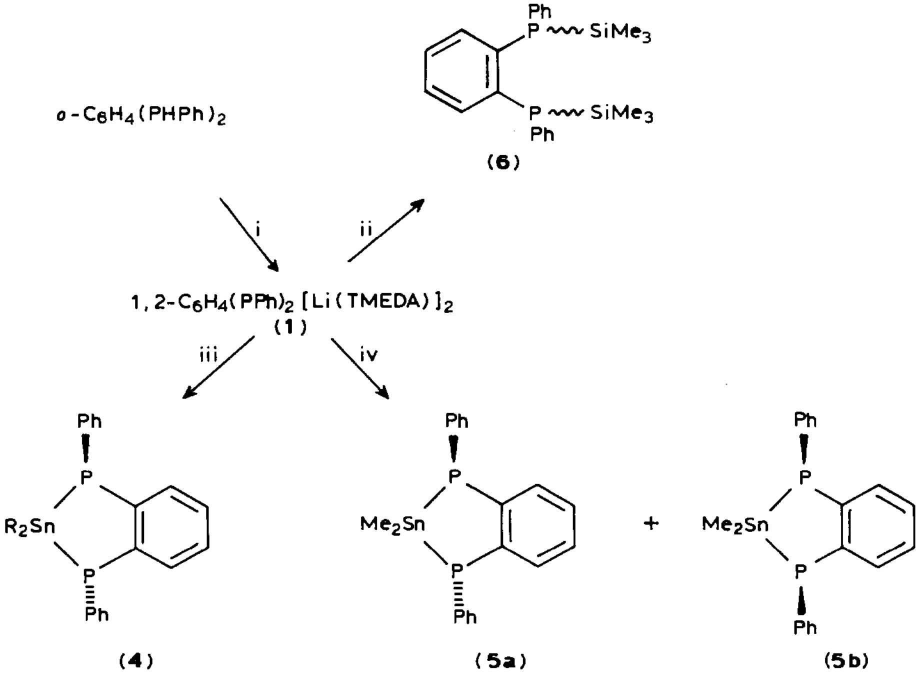
Selected bond distances (Å) and angles (°) in compounds **1** and **2**

Li–P		Li–P–Li		P–Li–P	
Compound 1					
Li(1)–P(1)	2.58(3)				
Li(2)–P(1)	2.55(3)	Li(1)–P(1)–Li(2)	103.4(9)	P(1)–Li(1)–P(2)	72(1)
Li(1)–P(2)	2.59(3)				
Li(2)–P(2)	2.59(3)	Li(1)–P(2)–Li(1)	102.0(9)	P(1)–Li(2)–P(2)	72(1)
Compound 2 [7]					
Li(1)–P(1)	2.57(1)				
Li(2)–P(1)	2.56(2)	Li(1)–P(1)–Li(2)	138.6(5)	P(1)–Li(1)–P(2)′	113.2(7)
Li(1)–P(2)′	2.57(2)				
Li(2)–P(2)	2.53(2)	Li(1)′–P(2)–Li(2)	128.7(5)	P(1)–Li(2)–P(2)	88.7(5)



(2)

in the crystal. Although this situation parallels that found for the di(organo)phosphidolithium compounds $[Li(\mu\text{-}PR'_2)]_2$ (R' = $CH(SiMe_3)_2$) [8] and $LiPPh_2(L)$ (L = TMEDA or PMDETA) [2b], the solution structures of compounds $[Li(PR_2)L_m]_n$ are sometimes complicated [9]. Likewise, the NMR data for **2** [12 *] were complex, and at first sight at variance with the structure in the crystal, which shows two types of Li atoms but apparently only one type of P atom. However, closer inspection of a molecular model shows that there are two different P sites, labelled P(1) and P(2) in



Scheme 1. The synthesis and some reactions of $1,2\text{-}C_6H_4(PPh)_2[Li(TMEDA)]_2$ (**1**, R = $CH(SiMe_3)_2$). Reaction conditions: i: $2LiBu^n$, 2TMEDA, $n\text{-}C_6H_{14}$, 0 °C; ii: $2SiClMe_3$, OEt_2, 0 °C; iii: $SnCl_2R_2$, OEt_2, 25 °C; iv: $SnCl_2Me_2$, OEt_2, 25 °C. Characterisation of compounds **1**–**6**: satisfactory C and H analyses, and NMR and X-ray (for **1** and **2**, Table 1) data.

2, as shown most obviously by the bond angles at these sites: Li(1)–P(1)–Li(2) 138.6(5)° and Li(1)′–P(2)–Li(2) 128.7(5)°. At 305 K, compound **2** in toluene-d_8 showed sharp $^{31}P\{^1H\}$ and $^7Li\{^1H\}$ singlets; but at 193 K, there were two Li signals each showing coupling to two equivalent phosphorus atoms, whereas there were two P signals each probably coupled to 2 Li's (2 broad signals) [12 *]. A plausible explanation of the low temperature solution spectrum is that it is consistent with structure **2**, in which Li(1) and Li(2) are not, but Li(1) and Li(1)′ are, rapidly exchanging [10a *]; this interpretation is also compatible with the ^{31}P and ^7Li solid state NMR data on **2** [10b *].

The compound $[\{Li(TMEDA)\}_2\{PhPCH_2CH_2PPh\}]_n$ (**3**), obtained from **2** + TMEDA, also showed complicated variable temperature NMR behaviour in THF [12 *]; its sparing solubility in PhMe, its high frequency $^7Li\{^1H\}$ signal, and a comparatively sharp $^{31}P\{^1H\}$ signal at low temperature are taken as indicative of the presence of a significant proportion of an ionic species.

We suggest that the diphosphidodilithium compounds **1** and **2** have much potential as sources of chelating or bridging 1,2-organobis(phenylphosphido)metal complexes, as illustrated in Scheme 1 for the former by the synthesis of some dialkyltin(IV) (**4** and **5**) or bis(trimethylsilyl) (**6**) derivatives, respectively. Diastereoselectivity is achievable when steric effects are substantial; e.g. for $R_2\overline{Sn[P(Ph)C_6H_4P}Ph\text{-}o]$ when R = $CH(SiMe_3)_2$ (**4**) but not when R = Me (*rac* (**5a**) (ca. 2/3) + *meso* (**5b**)) (ca. 1/3) (Scheme 1).

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10 Work in collaboration with A.G. Avent, R.K. Harris, G.A. Lawless, and A. Sabald; (a) 2D NOESY experiments; (b) solid state NMR experiments.

11 *Crystal data for 1*: $C_{30}H_{46}N_4Li_2P_2$, *M* 538.6, monoclinic, space group $P2_1/n$, *a* 17.246(3), *b* 10.835(3), *c* 19.399(3) Å; *β* 109.22(2)°, *U* 3422.9 Å^3, *Z* = 4, D_c 1.05 g cm^{-3}, Mo-K_α radiation, λ 0.71069 Å, *μ* 1.5 cm^{-1}. The structure of **1** was solved by direct methods and refined by full-matrix least squares to *R* = 0.13, *R′* = 0.12, with anisotropic temperature factors for atoms other than

carbon, using 1362 reflections with $|F^2| > \sigma(F^2)$. Atomic coordinates, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre; thermal parameters and structure factors are available from the authors.

12 Selected NMR data (^{31}P at 32.4 MHz (δ in ppm rel. to 85% H_3PO_4), ^{7}Li at 31.1 MHz (rel. to 5M LiBr), ^{119}Sn at 303 K and 134.3 MHz (rel. to $SnMe_4$), ^{1}H at 303 K and 360.1 MHz (rel. to $SiMe_4$)). **1** (Toluene-d_8): $^{31}P\{^1H\}$ at 203 K: δ −45.2 (binomial septet, $^1J(^{31}P-^7Li)$ 35 Hz); $^7Li\{^1H\}$ at 203 K: δ 0.7 (t, $^1J(^{31}P-^7Li)$ 37 Hz). **2** (Toluene-d_8): $^{31}P\{^1H\}$ at 303 K, −73.0 (s, $w_{1/2}$ 60 Hz); $^{31}P\{^1H\}$ at 193 K: −65.0 (s, $w_{1/2}$ 200 Hz), −72.0 (s, $w_{1/2}$ 260 Hz); $^7Li\{^1H\}$ at 303 K: 1.0 (s, $w_{1/2}$ 20 Hz); $^7Li\{^1H\}$ at 193 K: 1.4 (t, $^1J(^{31}P-^7Li)$ 38 Hz), 0.7 (t, $^1J(^{31}P-^7Li)$ 47 Hz). **3** (Thf/10% toluene-d_8): $^{31}P\{^1H\}$ at 303 K: −60.0 (s, $w_{1/2}$ 30 Hz); $^{31}P\{^1H\}$ at 193 K: −56.0 (s, $w_{1/2}$ 30 Hz), −59.0 (s, $w_{1/2}$ 250 Hz); −68.0 (s, $w_{1/2}$ 250 Hz); $^7Li\{^1H\}$ at 303 K: 0.5 (s, $w_{1/2}$ 15 Hz); $^7Li\{^1H\}$ at 193 K: 2.3 (s, $w_{1/2}$ 60 Hz) 0.2 (s, $w_{1/2}$ 60 Hz). **4** (Benzene-d_6 at 303 K): $^{31}P\{^1H\}$: −23.4 (s, $^1J(^{31}P-^{119}Sn)$ 892, $^1J(^{31}P-^{117}Sn)$ 856 Hz); $^{119}Sn\{^1H\}$: 52.5 (t, $^1J(^{31}P-^{119}Sn)$ 896 Hz). **5** (Benzene-d_6 at 303 K; peaks marked* refer to **5a**): $^{31}P\{^1H\}$: −43.4* ($^1J(^{31}P-^{119}Sn)$ 640 Hz), −50.3 ($^1J(^{31}P-^{119}Sn)$ 698 Hz); $^{119}Sn\{^1H\}$: +64* ($^1J(^{31}P-^{119}Sn)$ 639 Hz); +59.9 ($^1J(^{31}P-^{119}Sn)$ 695 Hz); ^{1}H: 6.95 (m, Ar*H*), 0.03 (s, $Sn(CH_3)$), 0.02* (s, $Sn(CH_3)$), −0.01 (s, $Sn(CH_3)$). **6** (Benzene-d_6 at 303 K): $^{31}P\{^1H\}$: −45.3, −45.9 ppm. Variable temperature data on *A* are complicated and will be reported later.